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**Thermodynamic and Kinetic Stability  
of Refractory Materials at Ultra-High Temperatures**

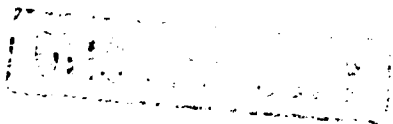
Annual Report for the Period

1 October 1989 - 30 September 1990

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

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**Thermodynamics and Kinetic Stability  
of Refractory Materials at Ultra-High Temperatures**

J. W. Hastie, D. W. Bonnell, and P. K. Schenck

Metallurgy Division

National Institute for Standards and Technology

**Introduction**

During this first contract year, work concentrated on initial measurements of vapor composition and associated gas temperature in two refractory systems using nanosecond timescale laser pulses to heat the solid refractories to ultra-high temperatures. Initial vaporization data for the hafnia (hafnium oxide,  $\text{HfO}_2$ ) system at 4900 K indicate surprisingly good agreement with extrapolations (mainly estimated) from the literature, both for absolute total pressure and individual vapor pressures. Similar measurements for the very complex vapor above  $\alpha$ -silicon carbide ( $\text{SiC}$ ) show poorer agreement with extrapolated lower temperature data. Several possible causes for this disagreement are discussed. One possible problem area, the indirect temperature scale, is being addressed, and preliminary surface temperature studies are discussed.

In both the cases reported here, it is significant that high temperature refractory materials such as hafnia and silicon carbide exhibit *equilibrium* vapor material-transport during and after heating by nominal energy loadings of  $10\text{-}100 \text{ J/cm}^2$  for 15 ns. This behavior is in contrast to the widely investigated laser desorption/ablation processes involving less

refractory ceramics, where ablation with a majority of material removal occurring via non-equilibrium processes is common.

### Technical Approach Summary

The basic methodology has been reported previously [1,2,3] in detail (see also the section, " Experimental Approach," in Appendix B. In summary, the approach is to use short pulsed heating of a refractory surface to vaporize a small representative sample of the material, and to provide an inertially confined containerless environment. Mass and optical spectrometry of the evolved gases are used to identify and characterize the vaporization process and the individual species comprising the vapor composition. Species partial vapor pressures are derived from the observed ion intensities through mass spectrometer (MS) calibration. The MS calibration process provides the means to relate measured intensities to absolute pressures. Direct determination of ion source sensitivities, mass spectrometer transmission, and the detector response function, each as a function of mass, is achieved using a gravimetrically prepared inert gas mixture. This mixture is introduced through a transpiration molecular beam source that has similar gasdynamic properties to the laser produced beams. Individual species electron impact ionization cross sections are estimated from atomic cross sections using a modification of the additivity rule. The vapor pressure results, combined with temperature information (see below), allow calculation of fundamental thermochemical values (heat and entropy of vaporization, free energies, condensed phase activities, etc.).

### Indirect Temperature Measurements

The MS data are obtained resolved in time as well as mass. We refer to the plot of MS intensity vs time of arrival as a Time-of-Arrival (TOA) plot (See Figure 1 in Appendix B - this figure is data taken 15° from the central axis of the emitted plume). When a characteristic arrival time for each species is plotted vs  $\text{mass}^{1/2}$ , a straight line indicates a common temperature origin for each species. This temperature is defined by the equipartition of translational energy expression,  $1/2Mv^2 = 3/2kT$ , which relates the translational velocity  $v$  of a species of mass  $M$  to the temperature of origin,  $T$ . Cast as a time relation, this expression becomes  $t \propto (d/3kT)^{1/2}M^{1/2}$ , where  $t$  is time,  $d$  is distance,  $k$  is Boltzmann's constant,  $T$  is temperature, and  $M$  is molecular mass. A linear relation between time-of-arrival and the square root of molecular weight (see for example, Figs 3 and 6 in Appendix B), provides compelling evidence that all the species fitting this relationship have a common temperature origin. It should be noted that, by the above equation, the fitted line must pass through the origin and all  $t$  vs.  $M^{1/2}$  plots are forced to pass through the origin. Our estimate for the instrumental delay indicates it is negligible on the timescale of neutral transit from the laser heated surface. We have found that half rise time of the leading edge of the TOA plot peak, or the peak centroid, or the peak maximum as the characteristic time can be used with similar results, when the calibration time is chosen in the same way.

Comparing time of arrival vs mass data from refractory compounds of interest with that from a graphite surface at known temperature, allows us to derive an *indirect* temperature for a given set of data. This procedure is discussed in more detail in references [1,4]. In

addition, where fundamental gas phase reactions are observed, known thermochemistry can be invoked to obtain another measure of temperature.

### **Accomplishments for FY-90**

During this reporting period, studies of both the SiC system and the HfO<sub>2</sub> system were begun. Although the present results still require refinement, they are sufficiently definitive, and of current interest, that an invited paper was prepared for the 1990 Electrochemical Society meeting in Seattle, Washington. A preprint of this paper is attached as Appendix B of this report, and a summary is given here.

#### **The HfO<sub>2</sub> System**

The initial measurements were made on surfaces of 99.9% CERAC/PURE\* monoclinic HfO<sub>2</sub> constructed from four 11 mm diameter by 2 mm thick tablets. The material was obtained in two forms, a white form, and a black modification labeled "oxygen-deficient." MS analysis showed no difference between the two forms, and CERAC\* indicated that the compositional difference was below the 99.9% purity limits. The white material turned black where struck by the vaporizing laser. For the present work, the black form was used. The vaporizing laser was a Nd/YAG system, producing typically 20 mJ, 15 ns pulses at the doubled 532 nm wavelength. A 50 cm lens focused the laser to a spot size about 250 × 1000 μm.

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Experimental runs were made with two sampling geometries. In the first orientation, the sample was placed flat so that the plume axis, which is normal to the surface, was coincident with the beam axis of the MS system. Time-of-Arrival spectra taken with this sampling mode showed mainly very fast peaks (120 - 160  $\mu$ s), typical of ions arising from the plume. Variable ionizing energy measurements for these peaks showed them to be independent of ionizing energy, confirming their assignment as ions. Only minor evidence was found for neutral species on axis. This result is in marked contrast to other systems studied. It should be noted that the MS system is inherently less sensitive, by a factor of the order of  $10^4$ , to neutrals, because of the ionization efficiency of the mass spectrometer ion source, than to ions produced externally which enter the ion source region. With the second sampling geometry, the sample mount was tilted at a  $15^\circ$  angle so that the MS molecular beam axis sampled the plume  $15^\circ$  from the axis normal to the surface. In this orientation, TOA plots showed arrival times corresponding to thermally produced neutrals (*e.g.* see Fig. 1 in Appendix B.). Variable electron energy measurements indicated that the slower arrival time peaks were neutrals, and a plot of time-of-arrival vs  $M^{1/2}$  for the neutrals (see Fig 3, Appendix B.) shows a common thermal origin for all observed neutral species. The indirect temperature derived from these data, relative to graphite under similar conditions, corresponds to a temperature of 4900 K. Although the  $O_2$  signal was small, and its time of arrival uncertain, the pressure ratio  $P(O\bullet)/P(O_2)$  ( $O\bullet$  = oxygen radical) is also in qualitative agreement with that expected due just to the dissociation reaction,  $O_2 = 2 O\bullet$  at a temperature somewhat above 4900 K. That the agreement is only qualitative is likely due to the uncertain  $O_2$  from  $O_2$ -deficient  $HfO_2$ , and the fact that  $O\bullet$  can arise from a number of

processes, including fragmentation from Hf-O species. However, this observation lends confirmation to the assigned indirect temperature determination.

Figure 4 of Appendix B shows laser vaporization vapor pressure data for the major Hf-O system species, plotted together with various literature data from Panish and Rief [5], estimates from Ackerman and Thorn [6], and extrapolations from the critically reviewed tabulations of Schick [7]. The box labeled "Equations" on the figure shows the reactions considered in interpreting the available literature data for comparison. The agreement is surprisingly good, considering that the literature data have been extrapolated to an absolute temperature almost twice the highest measured temperature, and to pressures 5 orders of magnitude greater. In addition, the range of extrapolation is several times the range of measured data. This clearly indicates that the Hf-O system is tractable to study by the LVMS technique, that there are no major unknown structure changes in the condensed phase at the higher temperatures, and that thermophysical data for HfO<sub>2</sub>, such as the heat of melting, are reasonable.

As encouraging as these preliminary data are, additional work remains before all the processes leading to laser HfO<sub>2</sub> vaporization are sufficiently well understood. In addition to refining the existing measurements, direct angular distribution measurements are planned.

### The SiC System

The silicon carbide chosen for this study is an  $\alpha$ -SiC, manufactured by Norton\*\* under

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the trade name Crystar. The material is greater than 99% pure alpha phase SiC. A metallographic examination showed no evidence whatever for free silicon anywhere in a cross-sectioned 19 mm diameter rod. Samples were prepared by sectioning the 19 mm bar into disks 2-3 mm thick with a diamond saw. The surface was prepared by surface grinding with a diamond wheel. The surface was cleaned by ultrasonic cleaning in alcohol, followed by thorough flushing with TFE electronic grade Freon.

As for  $\text{HfO}_2$ , sampling geometries included both on- and off-axis sampling. Unlike the Hf-O system, the SiC MS data both on-axis and off showed a preponderance of neutrals. The major difference between on- and off-axis data was the appearance of shoulders in the TOA plots at early times, indicative of some ion component on-axis. In no case did these early peaks indicate even as much as one percent ions. Variable ionization energy tests were used to confirm the assignments. Figure 6 of Appendix B shows a plot of TOA vs.  $M^{1/2}$ . All species are reported as the ion produced by electron impact ionization of neutral species from laser-heated SiC. The linear relationship involving every species is compelling evidence that (1) that all species come from a region at some specific temperature, and (2) all species were ionized (in the mass spectrometer ion source) predominately from the corresponding neutral. The first observation is based on the discussion above regarding translational temperature. The second is a corollary of the first. If the linear relationship between TOA and  $M^{1/2}$  implies a common origin temperature, and if some species were a fragment from a more massive neutral, it should arrive with a time indicative of the heavier neutral, as the mass analysis time is negligible. The indirect temperature derived from these measurements is  $42^{(n)} \pm 300$  K. The error limit is assigned based on fitting uncertainties

and our earlier analyses of measurement uncertainties (*cf.* [3]).

It is interesting to note that carbon species ( $C_1$ ,  $C_2$ , and  $C_3$ ) also obey this common temperature relation. Although the intensity ratios of  $C_{1-3}$  are quite insensitive to temperature, the time of arrival data are in excellent with the Si-C species. It is quite difficult to determine the presence of free carbon in carbides. The simplest test is metallographic examination, and there only a single phase ( $\alpha$ -SiC) was observed. From the observed pressures of  $C_2$  and  $C_3$ , combined with literature data from JANAF [8] for carbon vaporization from pure graphite, a value of 0.34 is obtained for the activity of carbon in SiC at the measurement temperature. This value is relatively independent of the value of  $T$  as the pressure ratio  $C_2/C_3$  is insensitive to temperature above 3000 K. This activity is consistent with the observation of no free carbon, and represents a reasonable value for the carbon activity in a carbide at such a high temperature.

When the SiC data are plotted together with JANAF [8] extrapolated values (assuming simple vaporization from condensed SiC to the noted vapor species), it is clear that the laser vaporization data disagree significantly with the extrapolation. There are several possible explanations.

First, the literature vaporization data on which the extrapolation is based are more uncertain, perhaps up to a factor of 10, than expected. Behrens and Rinehart [9] reported strong particle size effects at 2000 K, and reported higher pressures for all species than JANAF [8, see also second edition] selected. The particle size effect indicates an even lower accommodation coefficient for SiC vaporization than JANAF [8] considered. Although we feel that accommodation coefficient effects should be negligible by 4000 K, even in SiC, this

may not be the case. Our primary evidence for this is the observation that complex species ( $\text{SiC}_2$ ,  $\text{Si}_2\text{C}$ ) are still major components of the vapor. A low accommodation coefficient generally results in a strong discrimination against vaporizing complex molecules. It should also be noted that all the earlier data are from measurements with graphite Knudsen cells, with high carbon activity. Whether this is significant remains to be established.

A second explanation of the discrepancy is the argument that the decomposition mechanism under laser heating conditions (inertial confinement) may just be much different than static or oxidizing conditions due to complexity of vapor. We noted such an effect earlier in the BN system [4]. In that case, a more appropriate model under dynamic conditions suggested that the initial vapor process was the direct vaporization of  $\text{BN(g)}$ . This unstable gas molecule then decomposed under collision *in the gas phase*, yielding  $\text{N}_2$  and  $\text{B(g)}$ . Given the net flow of gas from the surface, and the very rapid expansion in vacuum,  $\text{B(g)}$  was never able to condense, thus producing an unexpected vaporization path. Our LVMS BN data fit that *local* equilibrium model well, and gave good agreement with existing thermochemical data. The SiC system is so complex, that if the problem is similar to BN in being due to an unusual vaporization process, selecting an appropriate model may be difficult.

Another possible difficulty is that the gasdynamics used for temperature scale may not match our calibrant systems. Although the variety of systems investigated so far (C, BN,  $\text{HfO}_2$ ) all show similar gasdynamics, the process is not yet well enough understood to ignore that possibility that extracting an indirect temperature via the process gasdynamics may be incorrect due to some unexpected inconsistency.

Finally, it is possible that the literature extrapolation is just not reasonable. The only evidence to counter that is SiC production experience with material transport, which is the basis for assigning 3250 K as the one-atmosphere decomposition pressure. Our results are still under analysis, and additional experiments are planned to attempt to resolve the above questions.

### Direct Temperature Measurements

The present experimental facility includes a gated Optical Multichannel Analyzer (OMA), which provides the capability for observing time-resolved (*ca.* 10 ns) emission over a wide portion of the visible spectrum. In addition to direct investigation of plume species by emission spectroscopy in support of the mass spectrometry work, the OMA technology offers a possible means to obtain direct measurements of the temperature of a laser-heated surface.

Our work on laser-produced emission spectra from graphite and silicon carbide targets indicate that line spectra often dominate the optical emission from the plume. The observation of direct spectra of the plume on a time-resolved basis has the potential for providing additional information regarding the plume temperature, but, as regards direct surface pyrometry, plume line emission is a strong interference which will clearly lead to erroneous results with almost any conceivable bandpass-type pyrometric system. A pyrometer based on OMA technology can, in principle, allow subtraction of line emission interferences as the measurements are taken.

The basis for this technique is the detection of a Planck black body radiation spectrum from the hot surface mixed with the plume line emission spectra. Assuming approximate

grey body emission characteristics (*i.e.* surface emissivity independent of, or a weak function of wave length), the radiation signature has the form:

$$R_{\lambda} = \frac{2\pi c^2 h}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

Figure 1 shows two normalized typical OMA spectra obtained from the surface of a graphite target irradiated by 1.06  $\mu\text{m}$  unfocused Nd/YAG laser pulses. An approximate array response curve has been used to correct the data. The sharp drop off in the data below 450 nm is due to optical losses in collection optics. The conditions have been deliberately chosen to

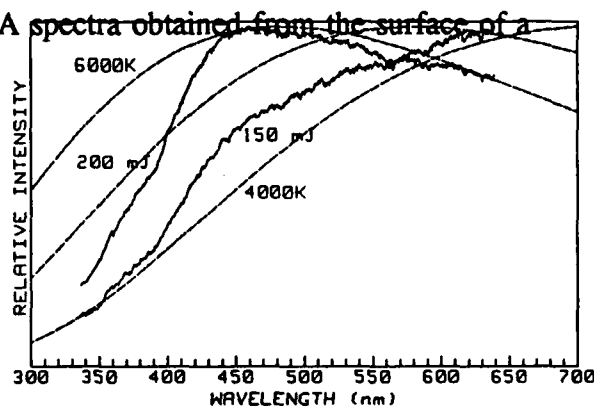


Figure 1. Normalized emission from graphite surface at two power loadings, and three calculated Planck law curves (dashed) showing temperature ranges.

minimize plume emission interferences. The dashed lines are normalized Planck function spectral calculations at the indicated temperatures, showing the surface emission to be approximately Planckian, and demonstrating feasibility of the method.

Figures 2 and 3 show time and spatially resolved spectra from a laser-irradiated (Nd/YAG, 532 nm,  $\sim 20$  mJ)  $\text{HfO}_2$  target. The OMA viewpoint is parallel to the surface, with vertical spatial resolution of 1 mm using slit defined 1:1 imaging. Figure 2 shows emission spectra as a function of time from just above the  $\text{HfO}_2$  surface. Qualitatively, the spectrum appears to show line emission features superimposed on a broadband background. Figure 3 shows the additional strong line emission in the ultraviolet from the plume at 1 mm

above the surface under the same conditions.

From these two figures we can see that there are two distinct emitting regions, and that their spectral signatures are very different, with the surface clearly emitting much longer wavelength radiation. It is not known whether the line structure observed is partially a result of reflecting the strong line emission from the plume, or is intrinsic to the surface region. It should be noted that the surface emission terminates much earlier than the plume, in qualitative agreement with expected cooling times of the surface. Also, the surface emission is much greater right after the end of the laser pulse. Further work is planned.

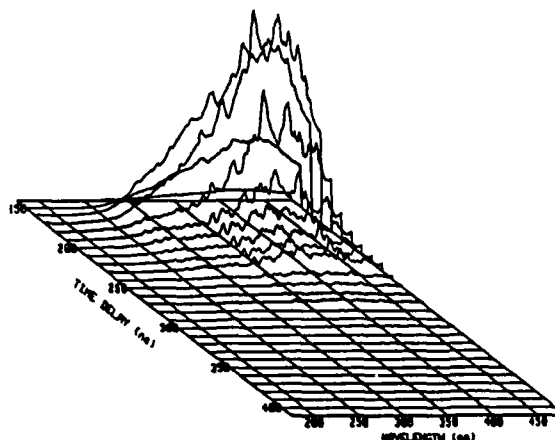


Figure 2. Emission spectra from laser-irradiated  $\text{HfO}_2$ , surface region. Relative vertical scale = 453932.

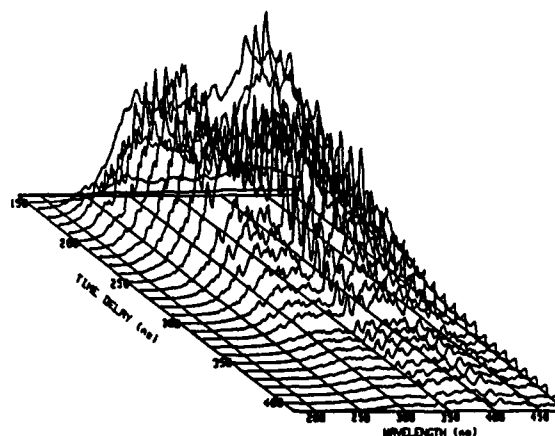


Figure 3 Emission spectra from laser-irradiated  $\text{HfO}_2$  at 1 mm above surface. Relative vertical scale = 37289.

## Summary

The application of Laser Vaporization Mass spectrometry to direct thermochemical measurements of refractories has been demonstrated for  $\text{HfO}_2$  and  $\text{SiC}$  refractories. In the



case of  $\text{HfO}_2$ , the highest melting refractory oxide, agreement between our species partial pressure data, obtained at 4900 K and the literature data extrapolated from below 3000 K is excellent. This is attributed to the relative simplicity of the  $\text{HfO}_2$  vaporization process. Remaining questions in this system center around the angular distribution of non-equilibrium ions produced by the laser impact. Our SiC data indicate that the ultra-high temperature vaporization process, predicted by extrapolating lower temperature literature data, is not reliable at temperatures well above the 3250 K "decomposition temperature" of SiC. A number of possible measurement problems are considered, and while a systematic error (particularly in temperature measurement) has not been completely ruled out, most of the usual problems appear unlikely explanations. Experiments are being planned to address these questions. At the present, we feel that the most likely explanation for the difference between the present measurements and the extrapolated lower temperature literature predictions lies in the simple assumptions made regarding the vaporization mechanism for the extremely complex vapor over SiC. This system thus appears to be a good test case for problems associated with extrapolating lower temperature thermochemical data to ultra-high temperatures.

## Future Work

### Work Plan for FY91-92

We intend to continue investigation of SiC and  $\text{HfO}_2$  in addition to other materials of interest, including  $\text{Ta}_x\text{C}$ ,  $x=1-2$ , MgO (an important refractory oxide), and other carbides,

oxides, and possibly nitrides. We will examine alternate forms (*e.g.* higher density SiC) and varied sampling geometries with a view toward improving our understanding of the questions raised in the preliminary work.

We are currently working on developing a direct temperature measurement capability using Optical Multichannel Analyzer-based optical spectroscopy. This will include setting up *in-situ* spectral response calibration facilities, identifying interference-free wavelengths, and work on the plume plasma temperatures and ion chemistry, which may be influencing the "frozen equilibrium" transfer of molecular species from the laser heating zone to the mass spectrometer. Development of an OMA-based pyrometry will allow for the comparison of directly measured surface temperature with indirectly (model) determined values for test materials.

Determining temperatures via energy models is still of considerable interest. We are working on an energy balance model, using heat loss calculations for vaporization, radiation, and condensed phase conduction processes. A major problem in modeling is estimating the energy loss to a radiation opaque plume, which may be a major process. We are looking at refining the model with direct inclusion of gas dynamics and material transport effects.

Switching laser operation to longer wavelengths (*e.g.* the 1060 nm Nd/YAG IR fundamental) will be investigated for several reasons. Using IR laser radiation shows promise for reaching even higher temperatures. IR laser light will make OMA-based pyrometry easier. Other modifications of the heating approaches we are considering include using the long pulse laser mode to change the experimental time scale.

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## **Appendix A.**

### **Publications and Presentations in 1989-1990 under AFOSR Sponsorship**

- "Ultra-High Temperature Laser Vaporization Mass Spectrometry of SiC and HfO<sub>2</sub>," D.W. Bonnell, P.K. Schenck, J.W. Hastie, and M. Joseph, in Proceedings of *Symposium on High Temperature Chemistry* (The Electrochemical Society, NJ, 1990).

## **Appendix B.**

**Ultra-High Temperature Laser Vaporization Mass Spectrometry of SiC and HfO<sub>2</sub>**

**D.W. Bonnell, P.K. Schenck, J.W. Hastie, and M. Joseph  
National Institute of Standards and Technology**

**Ultra-High Temperature Laser Vaporization  
Mass Spectrometry of SiC and HfO<sub>2</sub>**

D.W. Bonnell, P.K. Schenck, J.W. Hastie, and M. Joseph\*

National Institute of Standards and Technology  
Gaithersburg, MD 20899

\*NIST Guest Scientist

**ABSTRACT**

A Laser Vaporization Mass Spectrometric (LVMS) technique, demonstrated earlier for BN and C systems, has been applied to the systems SiC and HfO<sub>2</sub> at temperatures of 3500-5000°C. For certain conditions of laser energy, wavelength, pulse width, and plume sampling orientation, the species distributions appear to be thermally equilibrated and representative of the thermodynamic distribution at the hot surface. For SiC, the principal species were - Si, SiC, SiC<sub>2</sub>, Si<sub>2</sub>C, C, C<sub>2</sub>, C<sub>3</sub>, Si<sub>2</sub>, Si<sub>3</sub>, and for HfO<sub>2</sub> - Hf, O, HfO, HfO<sub>2</sub>, O<sub>2</sub>, in approximate order of decreasing abundance. Based on an indirect (beam velocity) temperature determination, the SiC vaporization rate appears to be much less than that based on an extrapolation of lower temperature Knudsen effusion data.

**INTRODUCTION**

Thermochemical data regarding vapor phase material transport of refractories at temperatures above 3000 K is quite sparse, generally being based on qualitative observations in poorly characterized environments, or on extrapolations of much lower temperature data using the Clausius-Clapeyron partial pressure-temperature relationship. Methods for obtaining equilibrium data are typically hampered by container interactions which are complex and hard to interpret. The requirement for quality high temperature data is a recognized need<sup>1</sup>. Areas as diverse as advanced ceramics, thermal stability, chemical vapor deposition (CVD) processing, design of protective coatings, and other very high temperature applications, need reliable species specific thermodynamic and kinetic data input to effectively model and understand the processes.

The use of laser energy as a means of high temperature surface excitation is an attractive technique for a variety of material transport processes, including thin film deposition, CVD, surface etching, cutting and welding. Three processes can occur: (1) laser desorption, where weakly bound surface species are directly removed from the surface by laser interaction; (2) laser vaporization, where the surface is heated thermally by the laser and approximately equilibrium vaporization occurs; (3) laser ablation, where multiple laser photons interact directly with strong chemical bonds, ejecting highly

energetic ions and neutral species with little relation to the system thermochemistry. An additional complicating factor is the interaction of the laser with the removed gases, giving additional ions and strong spectral line emissions. Both desorption and ablation are of interest to applications such as film deposition and etching. In this study, the laser is used primarily as a thermal source for ultra-high temperatures. We have previously shown<sup>2,3</sup> that the laser-induced vaporization technique can yield data which are representative of a Langmuir-type equilibrium process.

## EXPERIMENTAL APPROACH

In order to establish that thermal equilibrium vaporization conditions are obtained, it is necessary to examine the neutral vapor species in detail. For this purpose, we have developed a mass spectrometric facility, utilizing a quadrupole mass spectrometer (MS) with electron impact ionization for detection of neutral vapor species. The basic apparatus has been described in detail previously<sup>2,3</sup>. The laser used was a pulsed (10-30 mJ at 532 nm in  $\sim 15$  ns) Nd/YAG laser focused to approximately a  $300 \mu\text{m}^2$  spot size. The vaporized gas expands so rapidly to a non-interacting molecular flow condition that the neutral species partial pressure distribution is "frozen" during the plume-to-molecular beam transition. Thus, the molecular beam sampled from this region is representative of the vaporizing material<sup>2,3</sup>. The MS ion source is isolated by collimating apertures and is located 26 cm from the laser impact point. During a series of laser shots (typically 100-2000), the MS is tuned to an individual mass location, and the ion signal is accumulated in a signal averager or multichannel scaler (MCS) at  $1-5 \mu\text{s}$  per channel. The resultant *time-of-arrival* (TOA) profile (see Fig. 1) is a time-of-flight mass analysis of the quadrupole-selected signal. This TOA information is used to identify neutral precursors and to indicate establishment of local equilibrium among species. The sampling geometry is variable, with the molecular beam being selected either normal to the surface or at a  $15^\circ$  angle to the normal. The work reported here used the  $15^\circ$  off-normal sampling geometry.

### HfO<sub>2</sub> Results

Figure 2 shows mass spectral peaks obtained from vacuum deposition grade 99.9% monoclinic HfO<sub>2</sub> disks. The isotope ratios shown are in agreement with the expected pattern of Hf isotopes, which confirms the species identifications. Figure 3 shows a plot of TOA for various Hf, Hf-O, and oxygen species. That the O<sub>2</sub><sup>+</sup> peak does not fall on the line indicates that it could arise from a process cooler than the other Hf-O species (and O<sup>+</sup>), or possibly that it is an electron impact fragment ion (*e.g.* from HfO<sub>2</sub>). This peak was present at the limit of detection, with a signal to noise of perhaps 2:1; thus no conclusive interpretation is possible at this time. Figure 4 shows the Hf-O species vapor pressures. The data have been corrected for MS transmission mass-dependence, and the additivity approximation was used to estimate cross sections from atomic values. The temperature ( $4900 \pm 300$  K) was obtained indirectly by comparing Hf-O species TOA values with the TOA value of C<sub>2</sub> laser-vaporized from graphite at 4000 K, with gas-

dynamic conditions similar to the data of Fig. 3. The agreement between this reported species partial pressure data and that obtained by extrapolation of the literature<sup>4,5,6</sup> is excellent, indicating that the indirect temperature estimate is reasonable and that the vaporization process is occurring at nearly unit accommodation coefficient. These data are preliminary and more work is in progress, particularly with respect to obtaining more direct temperature information.

### SiC Results

Figure 5 shows an annotated mass spectrum from SiC (99% polycrystalline  $\alpha$ -SiC). The corresponding TOA plot for the various species is shown in Fig. 6. The linearity of the plot is remarkable, suggesting that the entire system is at local thermal equilibrium and that the identified species all arise predominately as parent ions. The various species noted, and their relative distributions have been observed previously at much lower temperatures<sup>5</sup>. Figure 7 shows corrected (as above) vapor pressures for the various species, plotted at the indirect temperature of  $4200 \pm 300$  K, determined in a manner similar to that described for  $\text{HfO}_2$  above. The agreement with the literature<sup>7</sup> is not particularly good. Several possibilities exist: (1) The temperature is approximately correct, but SiC vaporizes with a very low accommodation coefficient; (2) The indirect temperature is incorrect because the vapor production process is dramatically different from our other laser vaporization results, and the surface temperature was of the order of 3200-3400 K; (3) Linear extrapolation of low temperature data overestimates the vapor pressure dramatically; (4) For this particular material, the physical processes leading to vapor production under rapid laser heating are not similar to that occurring under continuous heating. (1) is unlikely, as, at the indicated temperature, surface bond strengths would have to be anomalously high. (2) is possible, and the relative species pressures suggest this as a possibility. The development of direct pyrometry on this time scale is in progress, with a view toward answering this question. The other two possibilities require experimental testing, which is in progress.

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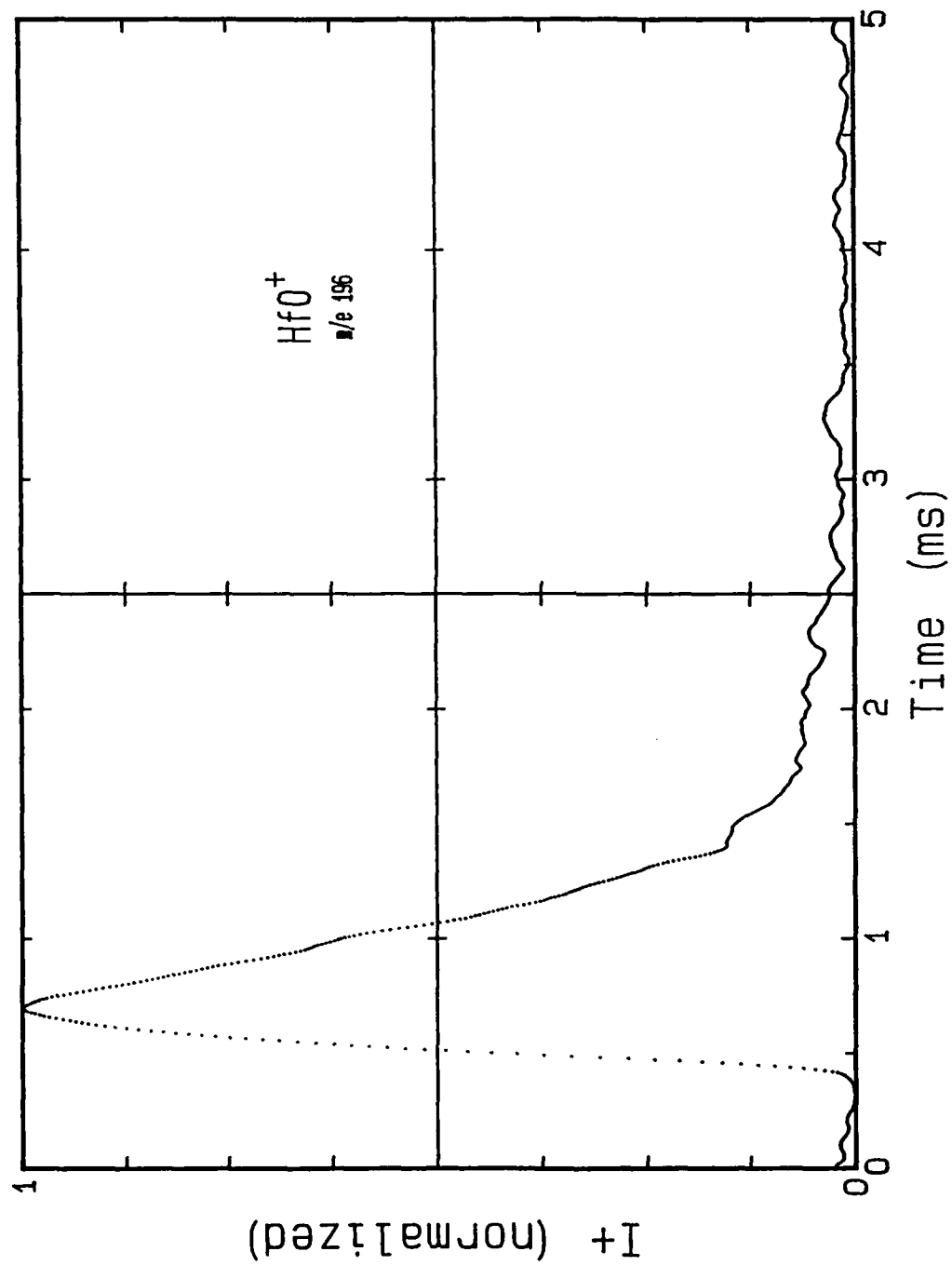


Figure 1. Time-of-Arrival (TOA) profile for the neutral species,  $\text{HfO}$ , detected by the quadrupole mass analyzer at  $m/e=196$  as the electron impact (20 eV) generated parent ion,  $\text{HfO}^+$ .



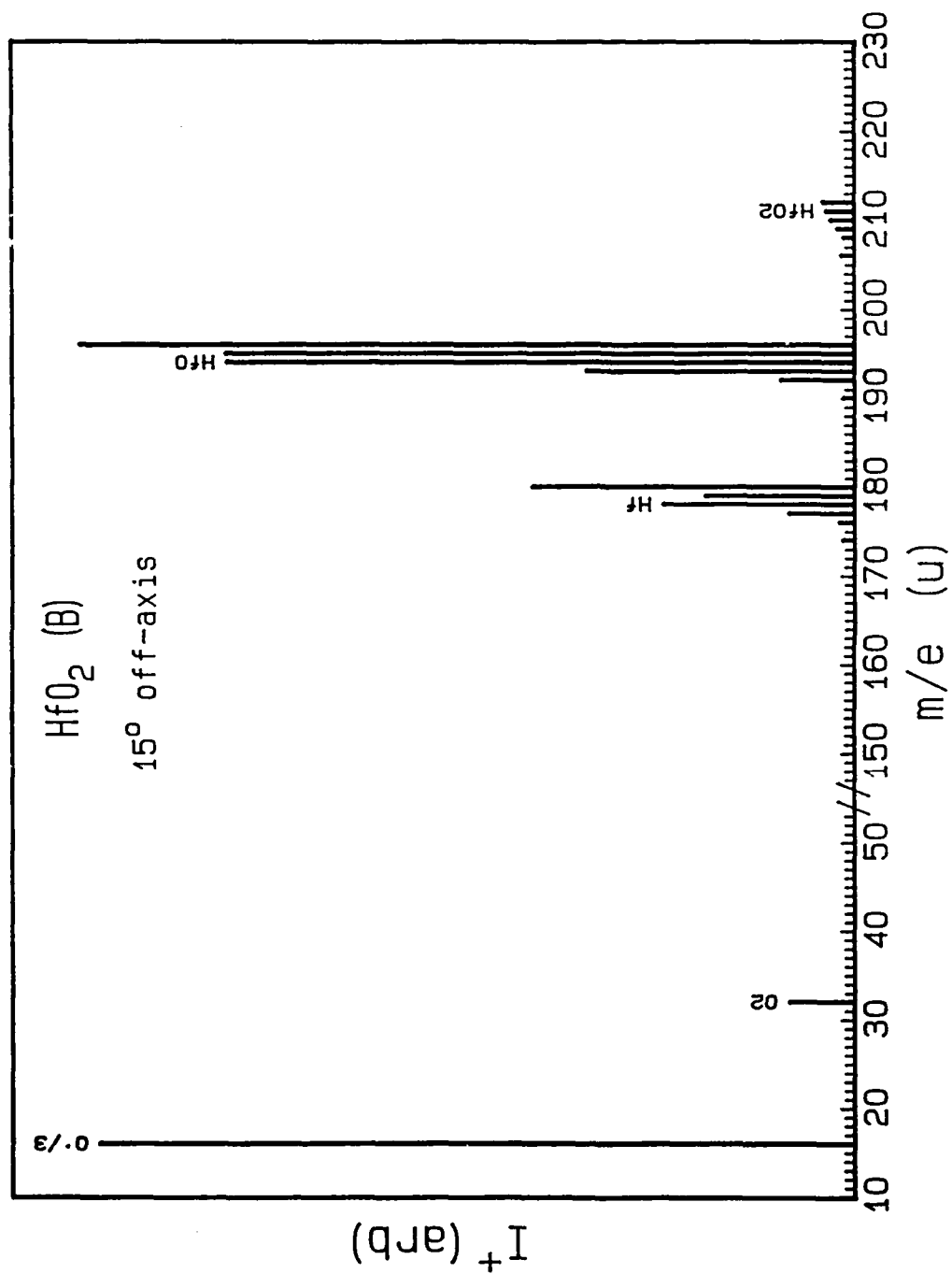


Figure 2. Mass Spectrum over  $\text{HfO}_2$  at 20 eV ionizing electron energy and  $T \sim 4900$  K.

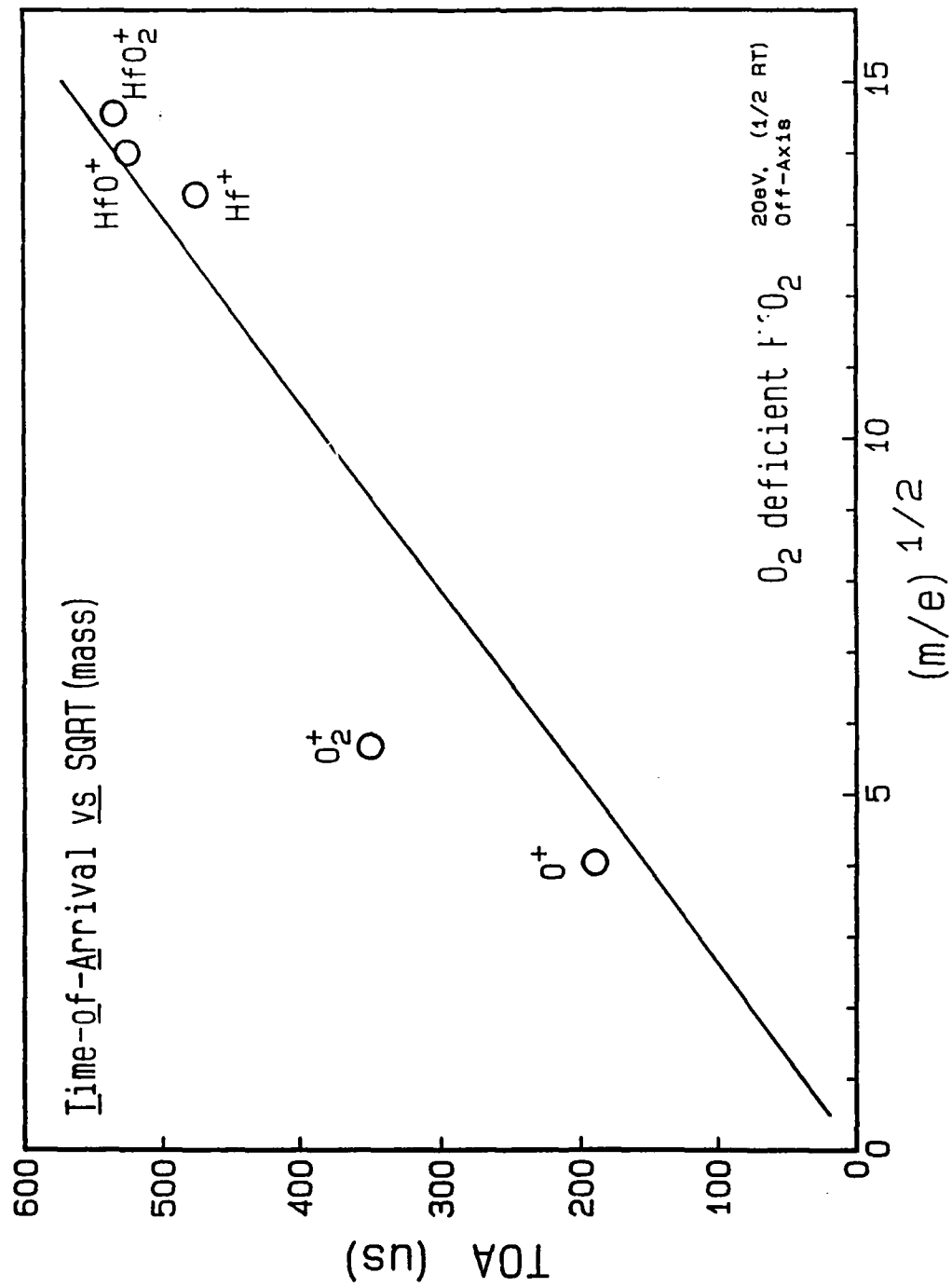


Figure 3. TOA plot for Hf-O species observed in Fig. 2.

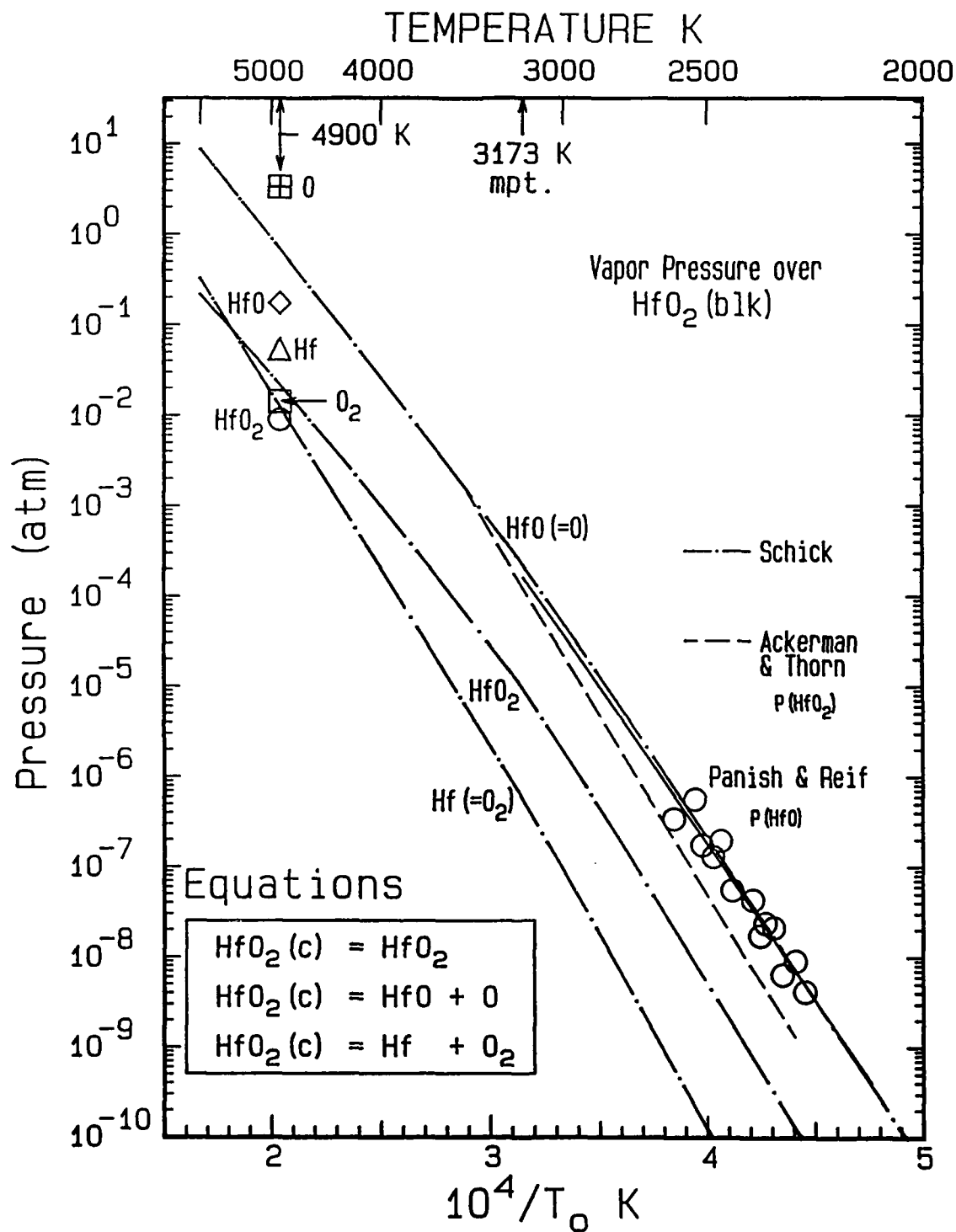


Figure 4. Vapor pressures of Hf-O species (symbols), plotted with literature extrapolations (curves).

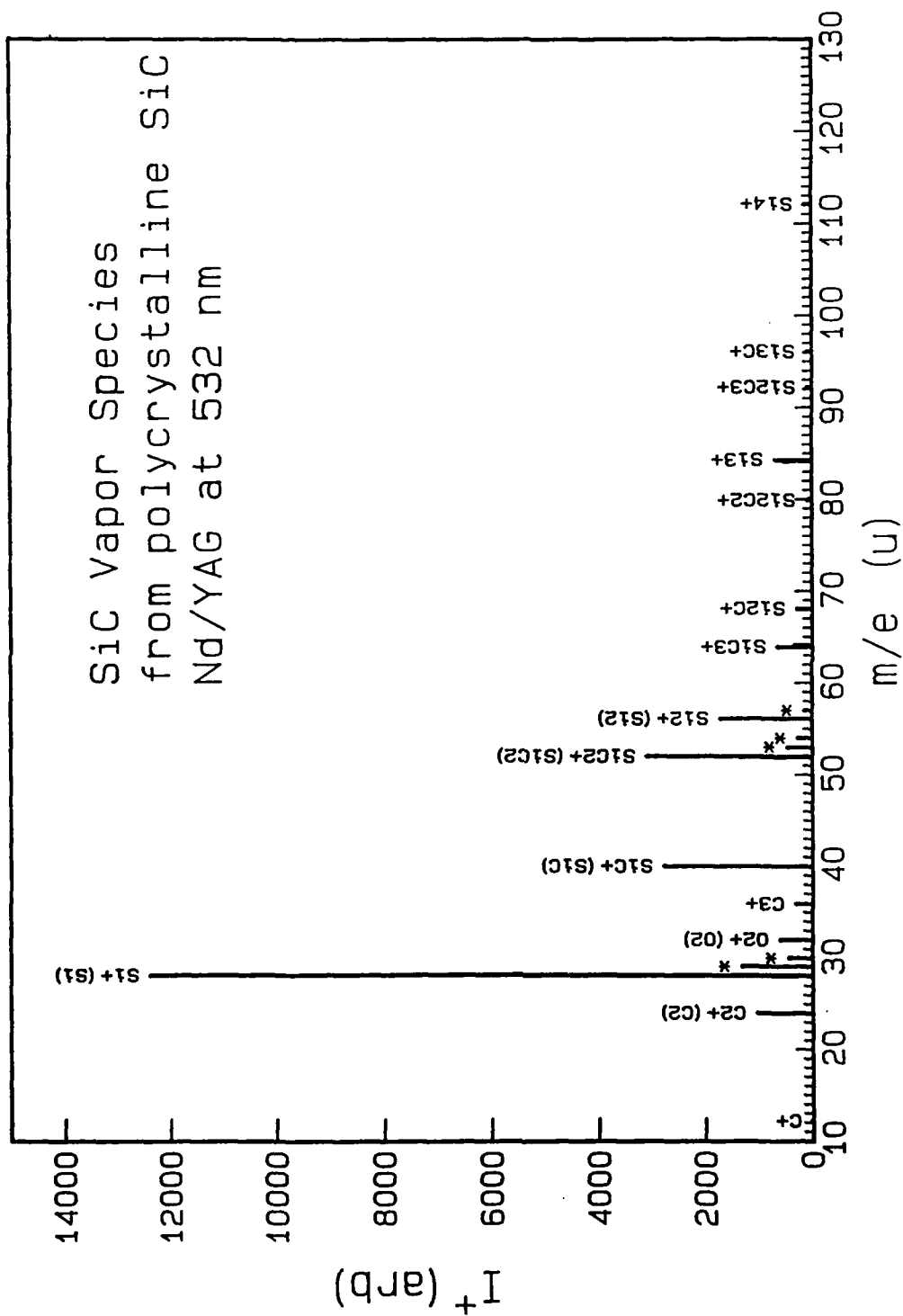


Figure 5. Mass Spectrum (16 eV) for Si-C species laser-vaporized from polycrystalline  $\alpha$ -silicon carbide.

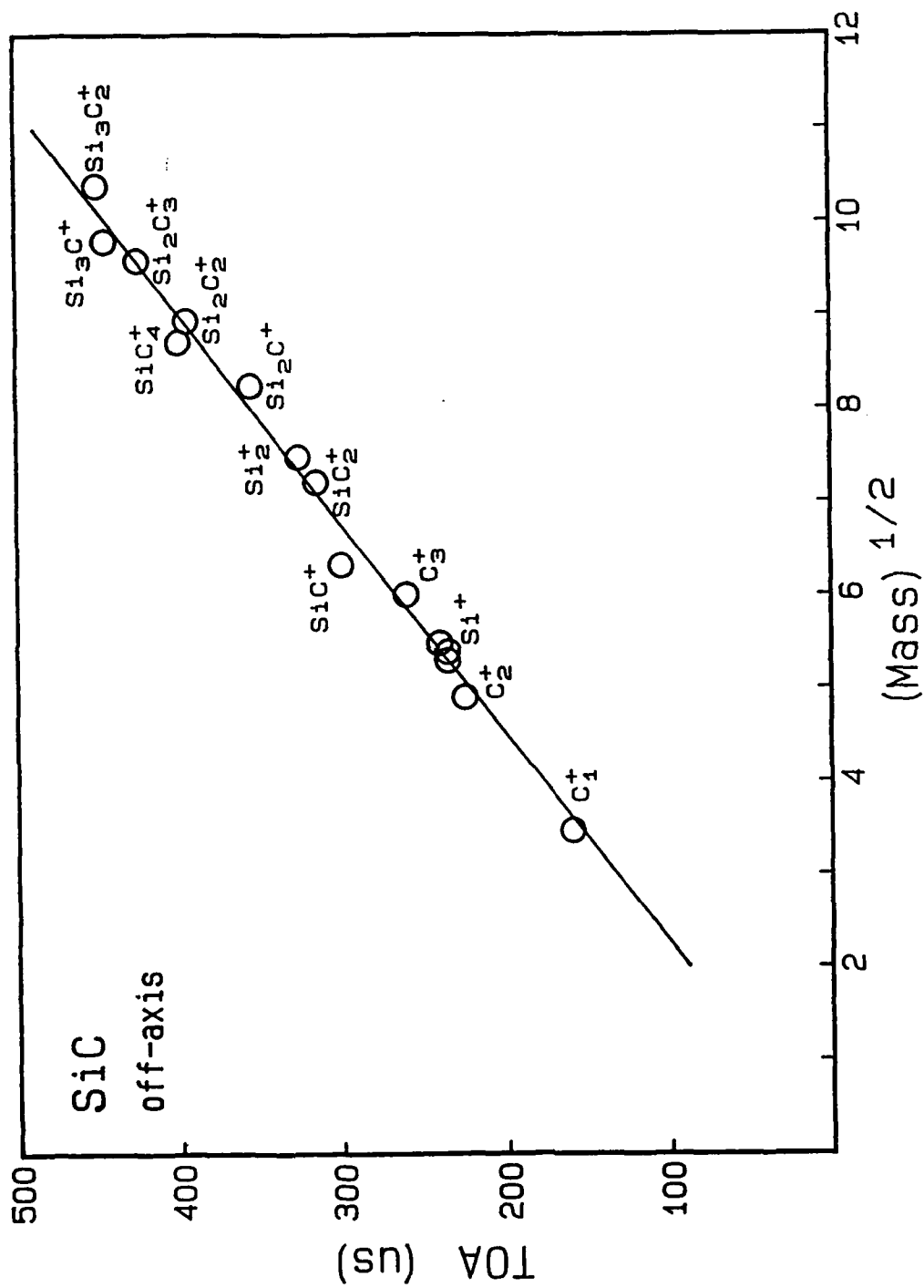


Figure 6. TOA plot for Si-C species (16 eV). Note that the C<sub>n</sub> species also follow the same line. The C<sub>2</sub>/C<sub>3</sub> species ratio corresponds to a carbon activity (relative to graphite) of about 0.38

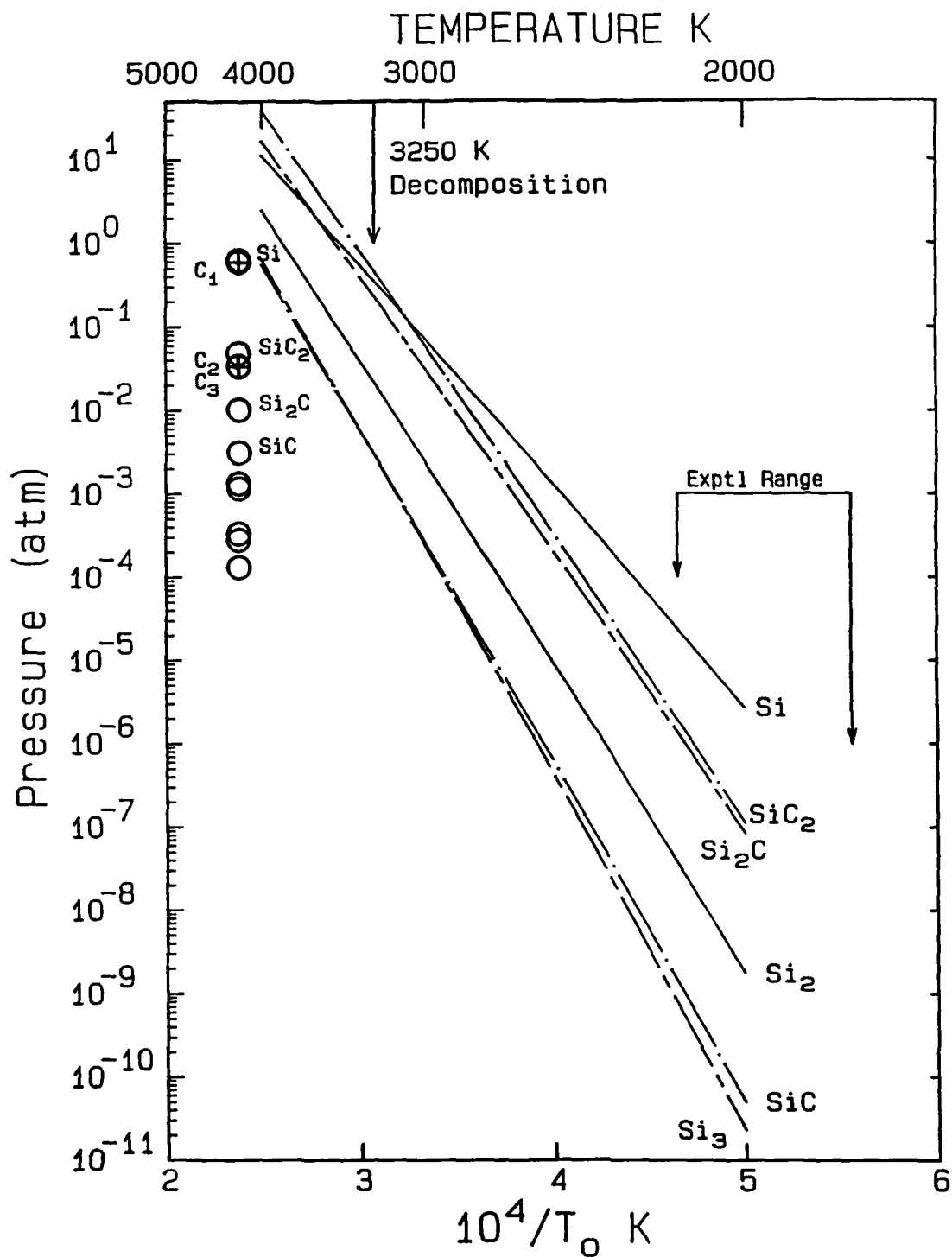


Figure 7. Vapor pressures of Si-C species (symbols), plotted with literature extrapolations (curves).